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[Hydrotris(1,2,4-triazolyl)borato]silver(I): Structure and Optical Properties of a Coordination Polymer Constructed from a Modified Poly(pyrazolyl)borate Ligand

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The replacement of the pyrazole rings (pz) in the popular poly(pyrazolyl)borate ligands,[1] $[H_nB(pz)_{4−n}]^−$, by e.g. 1,2,4-triazole or tetrazole leads to novel poly(triazolyl)- and -(tetrazolyl)borates which *can* bridge between metal centers, thereby creating coordination polymers with interesting solid-state structures and properties, whereas the versatile poly(pyrazolyl)borate ligands form exclusively molecular chelate complexes.[2]

We report here the synthesis, structure, and optical properties of [hydrotris(1,2,4-triazolyl)borato]silver(I) (**1**), which was obtained from the potassium salt of the ligand and AgNO₃ in water, followed by recrystallization from aqueous ammonia (eq 1).[3] Compound **1** presents itself as a two-dimensional coordination polymer according to the single-crystal X-ray analysis.[5] The metal−ligand coordination in **1** is detailed in Figure 1; Figure 2 illustrates the packing and the crystal morphology. In an unprecedented coordination mode[2] the hydrotris(triazolyl)borate ligand bis-chelates one silver center with two endodentate nitrogens and also bridges to two other silver atoms through two of the three exodentate nitrogen donors. Hence, in one triazolyl ring both nitrogens become utilized as donor atoms.

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(3) *Experimental:* A solution of 0.17 g (1.0 mmol) of AgNO₃ in 10 mL of water was overlayered with a solution of 0.26 g (1.0 mmol) of K[HB(C₂H₂N₃)₃][4] in 20 mL of water. Slow diffusion of the solutions led to the formation of a white amorphous precipitate which was recrystallized from aqueous ammonia (25%) to give air and moisture stable column-shaped colorless crystals (Yield: 320 mg, 60%; *m*p 232−234 °C (dec). C₆H₇AgBN₉ Calcd C, 22.25; H, 2.18; N, 38.92. Found C, 22.38; H, 2.47; N, 39.26).
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(5) *Crystal data of* **1**: Enraf-Nonius CAD4, ω−2θ scan (4.5 ≤ 2θ ≤ 55°), 293 K, Mo Kα radiation (λ = 0.71069 Å, graphite monochromator), 2581 reflections measured, 1316 independent (R_{int} = 0.0213), structure solution by direct methods. Refinement: full-matrix least squares on F^2; non-hydrogen atoms anisotropic; hydrogen atoms found and refined. Orthorhombic, $Pcn2_1$; nonstandard setting of $Pna2_1$ (No. 33), a = 13.030-(1) Å, b = 12.838(2) Å, c = 6.592(2) Å, V = 1102.7(4) Å³, ρ_{calcd} = 1.951 g cm⁻³, Z = 4, R1 = 0.0264, wR2 = 0.0622 for 1309 reflections [I > 2σ(I)] and 182 parameters, goodness-of-fit 1.027; largest difference peak and hole 0.675/−0.978 e Å⁻³. The absolute structure was determined on the basis of anomalous dispersion (Flack parameter[6] 0.01(5)). Full details can be found in the supporting information. Software packages used were *SHELXL-93* and *SHELXS-86* by G. M. Sheldrick.
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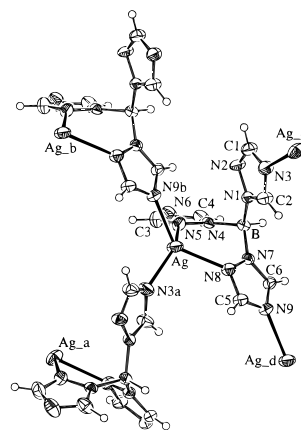
Figure 1. PLATON-TME plot[8] of the metal−ligand coordination in a fraction of the polymeric material of **1** (50% probability ellipsoids). Selected distances (Å) and angles (deg): Ag−N3a 2.264(3), Ag−N5 2.455(4), Ag−N8 2.379(6), Ag−N9b 2.310(6), N3a−Ag−N9b 111.0(2), N3a−Ag−N8 105.0(2), N9b−Ag−N8 136.7(1), N3a−Ag−N5 134.5(1), N9b−Ag−N5 88.3(2), N8−Ag−N5 83.0(2).
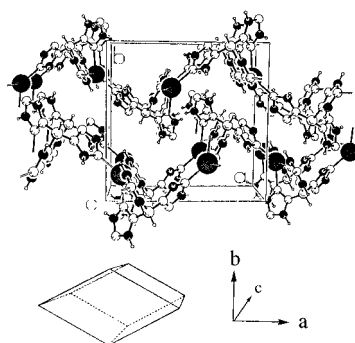

Figure 2. Packing diagram for the layer-type crystal structure of **1** (PLUTON[8]) and crystal morphology with relative positions of crystal axes from precession camera photographs. There are no short interlayer contacts.

The coordination sphere of silver is a strongly distorted tetrahedron. To the best of our knowledge, no [tris(*pyrazolyl*)borato]silver complex has been structurally characterized.[1,7]

$$K[HB(C_2H_2N_3)_3] + AgNO_3 \xrightarrow{H_2O/NH_3}$$

$$^2_\infty\{Ag[HB(C_2H_2N_3)_3]\} + KNO_3 \quad (1)$$
1
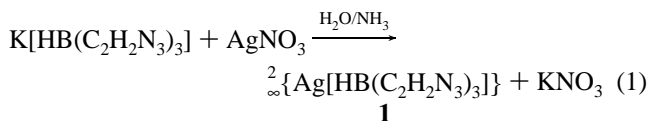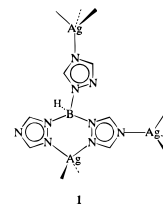
Compound **1** crystallizes in the acentric orthorhombic space group *Pna*2₁ which belongs to the crystal class *mm*2, where optical activity can occur as specific physical effects.[9] The tetrahedrally-coordinated silver and boron atoms have four

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different ligands, each, and are asymmetric centers. In the nonenantiomorphous class $mm2$ there exists, however, an equal number of R and S configured centers in the same crystal, and both optical axes in a single crystal of this optically biaxial orthorhombic system show rotation of the plane of polarization, however, with opposite sign.[10] Because of the dominant effect of double refraction, optical acitivity can only be measured along the optical axis in many crystal systems.[9,10] Determining the position of the optical axes requires in turn a rather detailed optical study. Therefore, verification of the single-crystal optical activity proved difficult here.

The birefringence of the crystal is also an important characteristic, and two of the indices have been determined using the prism method[10] exploiting the prismatic shape of the crystal. The measurement has been carried out with the incident laser beam propagating parallel to the crystallographic b-axis. The correct orientation was ensured by adjusting the crystal in such a way that the two different components of the beams penetrating the crystal result in symmetric refracted beams. The indices of refraction were determined at three different wavelengths to be $n_c = 1.661$, $n_a = 1.584$ at 532 nm, $n_c = 1.615$, $n_a = 1.581$ at 632 nm, and $n_c = 1.638$, $n_a = 1.567$ at 1064 nm (each with a systematic error of ± 0.005). No absorption peaks were found between 300 and 3000 nm. The refraction for light propagating along c was measured with a wavelength of 1550 nm on a single-crystal embedded in an epoxy resin and cut perpendicular to c into layers of ~ 50 and 100 μm (ab area about 0.13 mm^2). Because the crystal is birefringent, the velocity V of a light beam entering the crystal plate collinear to c is split into V_a and V_b, corresponding to the two indices of refraction n_a and n_b. Upon exiting the crystal plate, a phase difference $\delta = 2\pi d(n_a - n_b)/\lambda$ depending on the thickness of the crystal (d) and the wavelength (λ) is obtained. For three different thicknesses (to account for a possible factor of 2π), the phase differences were measured to give $\Delta n = n_b - n_a = 0.105(5)$ (at $\lambda = 1550$ nm). The magnitude of birefringence is comparable with very strong birefringent inorganic crystals, e.g. KNO_3 (1.3346, 1.5056, 1.5064).[10]

Furthermore, second-order nonlinear optical effects were investigated by optical second-harmonic generation (SHG). These investigations have also been done to prove properties connected with the determined symmetry group, in particular the lack of an inversion center. Experiments have been carried out with the fundamental ($\lambda = 1064$ nm) as well as the frequency-doubled ($\lambda = 532$ nm) output of a picosecond Nd: YAG laser. The SHG signal was detected by a photomultiplier and a gated integrator after passing a monochromator and appropriate filters.[11] Single crystals oriented with the b-axis parallel to the laser beam were used in these experiments.

For any polarization (i.e. in the a−c-plane for the chosen crystal orientation) of the incident fundamental beam, a SHG signal was found, which generally consists of two components polarized in the a- and c-directions with different intensities. In general, crystals of the symmetry group $Pna2_1$ may have seven independent $\chi^{(2)}$-tensor elements,[12] which for SHG experiments further reduce to 5 without and 3 if the Kleinmann conjuncture holds. At least the nonvanishing tensor components χ_{ccc}, χ_{aac}, and χ_{caa} contribute to the SHG signal. A first quantitative determination of the nonlinear susceptibility has been done only for χ_{ccc} so far, which can be expected to be the strongest component since the polar axis is along the c-direction. The coherence factor[13] describing the phase mismatch between the fundamental and the frequency-doubled beam was calculated as a spatial average across the beam diameter using the refractive indices $n_c(\omega)$ and $n_c(2\omega)$ as given above. It turned out that the maximum coherence factor was always close to the optimum value of 2 and obtained for symmetrical input (i.e. the beam axis coincides with the b-axis), in agreement with experimental observations. The SHG signal intensity averaged from three different samples was 2 W/cm^2 with an accuracy of about $\pm 20\%$ in these experiments. The second-order nonlinear optical coefficient can be evaluated from these results within the undepleted pump approximation to $d_{33} = \frac{1}{2}\chi_{ccc} = (6 \pm 3) \times 10^{-15}$ m/V. The large uncertainty is mainly given by the uncertinity of the dispersion $n_c(2\omega) - n_c(\omega)$ using the above-mentioned procedure. The determined nonlinear coefficient is in the same order of magnitude as for e.g. with quartz but clearly weaker compared with good SHG crystals like $KTiOPO_4$ or $LiNbO_3$.[13] Yet, **1** appears to be the first example of a poly-(azolyl)borate complex where the borate ligand and its metal connectivity are clearly the cause of the NLO effect.[14]

Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates and displacement parameters, and bond lengths and angles (6 pages). See any current masthead page for ordering and Internet access instructions.

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